Heavy ozone enrichments from ATMOS infrared solar spectra

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Abstract

Vertical enrichment profiles of stratospheric $^{16}O^{16}O^{18}O$ and 160180160 have been derived from space-based solar occult at ion spectra recorded at 0.01 cm-1 resolution with the ATMOS (Atmospheric Trace MOlecule Spectroscopy) Fourier-transform infrared (FTIR) spectrometer. The observations, made during the Spacelab 3 and ATLAS- 1, -2, and -3 shuttle missions, cover polar, mid-latitude and tropical regions. Between 26 to 2.6 mb inclusive ($\approx$25 to 41 km), average enrichments, weighted by molecular $^{48}O_3$ density, of(15i.6)% were found for $^{16}O^{16}O^{18}O$, (10±7)% for $^{16}O^{18}O^{16}O$, and (1 3±5)% for $^{50}O_3$ (10 standard deviation). Enrichments increased slightly with altitude, however no latitudinal variability was apparent. From a series of ground-based measurements by the ATMOS instrument at Table Mountain, California (34.4°N), an average total column $^{16}O^{16}O^{18}O$ enrichment of (17±4)% (1a standard deviation) was determined, with no significant seasonal variation discerned. Possible biases in the spectral intensities that affect the determination of absolute enrichments are discussed, However, any corrections to the these intensities would probably involve a scaling of the enrichments, and would not affect the observed lack of latitudinal and seasonal variability.

Introduction

Stratospheric enrichment of $^{50}O_3$ was first reported by *Mauersberger [1981]*, who found enrichments ranging from 0% to 40% using a balloon-borne mass spectrometer. (For the purposes of this paper, % enrichment = $[R_{obs}/R_{std} - 1] \times 100$, where R_{obs} is the observed abundance ratio of the heavy isotopomer to the regular isotopomer, and R_{std} is the standard ratio. For $^{50}O_3$ enrichment, $R_{std} = 5.97 \times 10^{-3}$, or three times the natural abundance ratio of ^{18}O to ^{16}O, ignoring a very small abundance of $^{16}O^{17}O^{17}O$. See *IUPAC, [1983]*). Further stratospheric enrichment of $^{50}O_3$ have been reported based on mass spectrometry *[Mauersberger, 1987]*, far-infrared emission spectroscopy *[Abbas et al., 1987; Carli and Park, 1988]*, and cryogenic grab-sampling followed by mass-spectrometry *[Schueler et al., 1990]*. These measurements have sometimes shown little consistency with each other. Figure 1 summarizes previous measurements of $^{50}O_3$ enrichment profiles as well as averaged results of the analyses presented here. Column enrichments have also been determined using mid-infrared solar-absorption Fourier-transform spectrometry. *Rinsland et al. [1985]* determined a column enrichment of $(11 \pm 11)\%$ and $(5 \pm 7)\%$ for $^{16}O^{16}O^{18}O$ and $^{16}O^{18}O^{16}O$, respectively. *Goldman et al.* [1989], from two balloon-based observations, found column enrichments above 37 km of $(20^*14)\%$ and $(40 \pm 18)\%$ for $^{16}O^{16}O^{18}O$, and $(1658)\%$ and $(25 \pm 12)\%$ for $^{16}O^{18}O^{16}O$. Enrichment of $^{50}O_3$ from about 8 to 10% in tropospheric urban air was reported by *Krankowsky et al. [1995]* who found no apparent variation in the enrichment with tropospheric O_3 mixing ratios,

Heavy ozone enrichment has also been observed in laboratory measurements. *Anderson et al. [1989]* found ozone created using an electric discharge (which can produce excited states of O and O_2) enriched primarily in the asymmetric isotopomers, such as $^{16}O^{16}O^{18}O$. *Morton et al. [1990]* found that enrichment can occur via the reaction of ground-state atomic and molecular oxygen,

$O(^3P) + O_2(^3\Sigma_g) + M \rightarrow O_3 + M$, the so-called Chapman formation reaction, and under these conditions, *Mauersberger et al.* [1993] found enrichment *totally* in the asymmetric isotopomers. *Miller et al.* [1994] proposed that the reaction of vibrationally hot O_2 ($v \gtrsim 26$) with another O_2 molecule can lead to heavy ozone enrichment via preferential potential energy curve-crossing of heteronuclear O_2 from the $O_2(^1\Delta_g)$ to the $O_2(^3\Sigma_g)$ state (see *Valentini* [1987]). however, appreciable production of such vibrationally hot O_2 was predicted to occur only above about 35 km, and the enrichment produced less than 5% at 40 km.

While Miller et al. may have provided an explanation for some of the enrichment in the mid-stratosphere, the bulk of the enrichment lacks a generally accepted theoretical explanation. indeed, detailed statistical mechanical analyses by *Kaye and Strobel [1983]* and *Kaye* [1986] predicted a slight *depletion* of $^{50}O_3$ under stratospheric conditions. This discrepancy between observation and theory indicates that current understanding of ozone formation is incomplete (see, for example, *Anderson et al.* [1992]). However, a promising advance in finding an enrichment mechanism is the recent discovery of several electronically excited states of ozone near the dissociation threshold *[Anderson and Mauersberger, 1995]*. It may be possible that the formation of ozone via the Chapman mechanism goes through one or more of these states whose quantum properties (such as lifetime) are dependent on the isotopic composition of the reactants.

From Figure 1, it is difficult to discern any consistent vertical gradients in previously published measurements, and data are lacking on either seasonal or latitudinal effects in the stratosphere. In this study, we take advantage of the high vertical and latitudinal range of the ATMOS data set from the Spacelab3 and ATLAS series missions to determine if there are substantial vertical or latitudinal gradients. We also evaluate the $^{16}O^{16}O^{18}O$ column enrichments from ground-based spectra from Table Mountain Facility (TM F), Wrightwood, CA, (34.4°N, 117.7"W, 2.2 km altitude) to determine if there is a seasonal variation.

Data Acquisition

Information about the ATMOS instrument and its use on the shuttle can be found in *Gunson et al.* [this issue]. The spectral filters used for analyses described here, filters 1,9 and 12, had ranges of 650-1100 cm^{-1}, 650-2450 cm^{-1}, and 625-1400 cm^{-1} respective] y. The number of vertical profiles used for this study were 4 from Spacelab 3, 39 from AT1 .AS- 1,29 from ATLAS-2 and 87 from ATLAS-3, Using the ATMOS instrument from Table Mountain Facility, ground-based total column measurements were made on 48 separate days from October, 1985 through July, 1990, usually at solar zenith angles corresponding to about 1,5 and 10 airmasses. As the ATMOS instrument has a very fast response time (2.2 seconds pcr scan), between 8 and41 successive, double-sided interferograms were able to be taken within a narrow range of solar zenith angles, which, after transformation and averaging, produced spectra with a signal-to-noise ratio of at least 280 to 1. Only data taken in the morning from TMF were analyzed, as tropospheric smog from nearby Los **Angeles** could be advected over the intervening mountains and over the site in the afternoon [scc *McDermid and Walsh,* 1991].

Data Analysis

ATMOS analysis techniques for space-based observations have been described by *Norton and Rinsland [* 1991]. (See also *Gunson et al.* [this issue] on the analyses of $^{4*}0_3$ from ATMOS space-based observation s.) The narrow, unresolved ν_1 band Q-branch centered at 109035 cm-l was anal yzed for $^{16}O^{16}O^{18}0_0$, as were several lines of the ν_3 band P-branch for $^{1}60'8_0 {}^{16}O$ (see Figure 2 and Table 1). Interfering $^{48}0_3$ lines were fitted before final fitting of $^{16}O^{18}O^{16}O$ or $^{16}O^{16}O^{18}O$ was attempted. It was not possible to usc all of the $^{16}O^{16}O^{18}O$ and $^{16}0'80]60$ features used by *Rinsland et al. [1985]* and *Goldman et al. [1989]* because, at the spectral resolution of the ATMOS instrument, there was too much interference by other molecules to successful] y fit some of the heavy ozone lines. Analyses of enrichments were made in between

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tangent pressures of 2.6 and 26 mb because only in this region could suitable lines be found that simultaneously had reasonable signal above the noise, were unsaturated and reasonably free from interference by other molecules. Spectral parameters for all lines were from the ATMOS line] ist [*Brown et al.*, **1995**], which currently incorporates the ozone parameters given by *Flaud et al.* **[1990].** Error sources for stratospheric measurements are discussed by *Gunson et al.* [this issue], although wc note here that the systematic error caused by uncertainties in the line intensities are 4% for $^{48}O_3$, 20% for $^{16}O^{16}O^{18}O$ and 10% for $^{16}O^{18}O^{16}O$.

The analysis procedure for the TMF ground-based retrievals differed in that an assumed vertical ozone mixing ratio profile was scaled by a single multiplicative factor until a best fit was obtained bet wccn observed and calculated spectra. Table 2 describes the lines used for TMF retrievals. Assumed vertical ozone profiles were created using month] y-averaged profiles from the JPL Lidar on TMF [*McDermid*, 1993]. Vertical temperature and pressure profiles were adapted from daily National Meteorological Center data and merged with the U.S. Standard Atmosphere [1976] for higher altitudes. These profiles were then adjusted so that the atmosphere was in hydrostatic equilibrium. To achieve better consistency in the retrievals among the different airmasscs sampled within a day, the height registration of the assumed ozone profiles was shifted up or down 0-3 km. In a similar fashion to the spaced-based measurements, neighboring lines of $^{48}O_3$, CO_2 and H_2O were fitted before final fitting of the [1]"0160' *O absorption was attempted. Measurement of column $^{48}O_3$ by the ATMOS instrument at TMF was previously reported by *Gunson and Irion* [1991], however, as some of the $^{48}O_3$ lines used in that study may have been saturated at high airmasscs, the $^{48}O_3$ columns have been rc- analyzed for this study, The $^{16}O^{18}O^{16}O$ column from TMF was not retrieved because interference by neighboring $^{48}0_3$, H_2O and CO_2 lines was too large to achieve acceptable fits, Error sources for the TMF retrievals are listed in Table 3.

It should be noted that in the determination of the $^{16}O^{16}O^{1}$'O line intensities by *Camy-Peyret et al.* [**1986**]**, and incorporated into the ATMOS spectral linelist *[Brown et al.,* 1995], the concentration of '$^{6}0^{16}0$'80 in the sample cell was not directly measured. Rather, the line intensities of $^{16}0^{1}80$'60 were derived from theory, and the $^{16}O^{18}O^{16}O$ concentration in the sample cell calculated from measurement of the spectral lines, The '%1%'8^{0} concentration was then assumed to be twice that of '$^{6}0$' $^{8}0^{16}0$ [see *Flaud et al., 1986].* This makes an implicit assumption that any enrichment of $^{16}O^{16}O^{18}O$ and $^{16}O^{18}O^{16}O$ would be equal. Camy-Peyret et al. produced their ozone sample using an electric discharge in a liquid-N_2 cooled vessel. However, in subsequent production of heavy ozone by *Anderson et al. [1989],* also using an electric discharge, but at room temperature, the $^{16}O^{16}0^{1}80$ produced carried about t wice the enrichment of $^{16}O^{18}O^{16}O$. It is thus possible that the heavy ozone sample used by Camy-Peyret et al. had a $^{16}O^{16}O^{18}O$ to $^{16}0^{18}0^{16}0$ abundance ratio greater than 2:1, so the line intensities derived for $^{16}0^{16}0$'80 may have been systematical] y over-estimated, resulting in an under-estimated '$6_{0}160$'80 abundance when these parameters are used for stratospheric spectra. (We note, however, that the effect of the different reaction temperatures of the Anderson et al. and Camy-Peyret et al, experiments on the enrichment partitioning bet ween $^{16}O^{16}O^{18}O$ and $^{16}O^{18}O^{16}O$ is not known.) If wc assume that the $^{50}0_{3}$ enrichment in the Cam y-Peyret et al. experiment was 4% (in the upper range of the enrichments found by *Heidenreich and Thiemens [1983]* under similar conditions) and the enriched $^{16}0^{16}0$'80-160180$^{1}_{6}0$ partitioning of the was 4:1 (as in *Anderson et al. [1989]),* then the error in the $^{16}O^{16}O^{18}O$ line intensities caused by assuming a 2:1 partitioning is a relatively small 2%.

Results

Figure 3 illustrates vertical enrichment profiles for $^{1}601601$ ^{8}O and $^{16}O^{18}O^{16}O$, averaged within latitude bands covered by ATMOS over four shuttle missions. At least three measurements were used to calculate each datum point. The enrichment profiles tend to increase slightly with

altitude, and while the standard deviations can be quite high, there does not appear to be any systematic latitudinal variations. Figure 1 illustrates previous] y published $^{50}O_3$ enrichment measurements and the average ATMOS $^{50}O_3$ enrichment profile (assumed the sum of one-third the $^{16}O^{18}O^{16}O$ enrichment and two-thirds the $^{16}O^{16}O^{18}O$ enrichment). The ATMOS average profile was determined by averaging results across constant pressure surfaces and assigning an approximate alt itude. Weighted by the $^{48}O_3$ density, the globally averaged $^{50}O_3$ bet ween 2.6 and 26 mb inclusive is (13±5) %, while that for $^{16}O^{16}O^{18}O$ and $^{16}O^{18}O^{16}O$ arc (15±6)% and (10±7)%, respectively (1 σ standard deviation).

Figure 4 shows the $^{16}O^{16}O^{16}O$ columns measured above TMF. The random error for the $^{16}O^{16}O^{18}O$ enrichment data points (lower panel) is, on average, 9%. While the ozone column varies substantially, no seasonal variation in the enrichment can be discerned. This is in qualitative agreement with a lack of variability in tropospheric $^{50}O_3$ enrichments found by *Krankowsky et al.* [1995], Ignoring systematic error, the average column enrichment is (17±4)% (1 σ standard deviation), in good agreement with the $^{16}O^{16}O^{18}O$ enrichment derived from the ATMOS stratospheric profiles.

Conclusions

We have analyzed ATMOS stratospheric spectra for the enrichments of '60'60'80 and $^{16}O^{18}O^{16}O$, and ground-based spectra for the column enrichment of $^{16}O^{16}O^{18}O$. We can find no discernable seasonal variability in the $^{16}O^{16}O^{18}O$ column enrichment, nor can any latitudinal variation be detected in the vertical enrichment profiles. T] ıere appears to be a slight increase with altitude, possibly an effect of increasing temperatures and/or decreasing, pressure. These observations suggest the enrichment of heav y ozone in the stratosphere is relatively constant, and only weak] y regulated by temperature and pressure.

Although previous studies have not ruled out other enrichment processes, laboratory measurements have shown the most significant enrichment in the Chapman reaction, with O and

O_2 in the electronic ground state. Noting that the Chapman mechanism has been shown to produce no enrichment for the $^{16}O^{18}O^{16}O$ isotopomer, our determination of a $^{16}O^{18}O^{16}O$ enrichment of $(10\pm7)\%$ (1 σ standard deviation) suggests that the $^{16}O^{18}O^{16}O$ line intensities may be biased too low by 10% with respect to the line intensities of $^{4X}O_3$. This is within the expected systematic error, although we note it may be possible that other unknown processes are operating to enrich stratospheric '6O' $^{8}O^{16}O$, much as ozone produced in an electric discharge becomes enriched in $^{16}O^{18}O^{16}O$. Furthermore, since the $^{16}O^{16}O^{18}O$ line intensities derived by *Camy-Peyret et al.* [1986] were determined making use of the $^{16}O^{18}O^{16}O$ line intensities, the $^{16}O^{16}O^{18}O$ line intensities may also be too low, Laboratory measurement of the $^{16}O^{16}O^{18}O$ and '6O18O18O spectral line intensities are necessary for verification of the absolute stratospheric enrichments described here. Since *Flaud et al. [1986]* and *Camy-Peyret et al.*[1986] reported good model fittings to their laboratory spectra, such laboratory measurements would probably produce a constant, corrective scaling of the line intensities (and thus the enrichments), but would not affect the precision of the results described here.

Acknowledgements

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Table 1: Spectral intervals used for heavy ozone profile analyses from space

Molecule	Window center frequency (cm^{-1})	window width (cm^{-1})	Line center(s) (cm^{-1})	Line intensity (cm molecule^{-1}) at 296 K	Ground state energy (cm^{-1})	Temperature sensitivity of intensity (%/K at 220K)
$^{16}O^{16}O^{18}O$	1090.445	0.55	unresolved	2.14×10^{-23} (a)	203 (b)	-0.1
	975.27	0.12	975.2503	1.69×10^{-24}	546	1.0
			975.2838	$2.30_x 10^{-24}$	495	0.7
	981.715	0.14	981.6756	$3.s4 \times 10^{-'24}$	363	0.4
			981.7107	4.46×10^{-24}	328	0.3
16(3180160"	985.09	0.44	984.9062	4.32×10^{-23}	2.98	0.2
			984.9790	5.48×10^{-23}	2.64	0.1
			985.0321	$2.20 X 10^{-23}$	395	0.5
			985.1031	4.78×10^{-23}	279	0.1
			985.1578	$3.32 X 10^{-23}$	334	0.3
			985,2171	$5.lox 10^{-23}$	268	0.1
	990.422	0.14	990.3889	$1.55x 10^{-23}$	593	1.3
			990.3895	1.74×10^{-23}	567	1.3
			990.3918	1.74×10^{-23}	567	1.1

Notes:
(a) Sum of intensities between 1090.1 and 1090.6 cm^{-1}
(b) Average weighted by the intensity of the individual lines.

Table 2: Spectral intervals used for column density analyses from 'l'able Mountain

Molecule	Line Center (a) (cm-1)	Line Intensity (x 1022 cm molec.$^{-1}$)	Ground State Energy (cm^{-1})	Temperature Sensitivity of Intensity %/K at 220K	Airmass Range
16(3160160	1095.1008	5.19	310.3	0.2	<1.5
	1114.8233	1.03	77.1	-0.5	3-10
	1123,4234	6.85	120.3	-0.4	<3
	1126.2511	2.49	42.9	-0.5	<5
	1140.9448	1.02	190.2	-0.1	3-10
	1163.4222	2.57	253.9	0.04	<5
	1176.1047	1.41	353.3	0.3	3-10
$^{16}O^{16}O^{18}O$	(b)	2.14(c)	203 (d)	-0.1 (d)	all

Notes:
(a) Interval width for all $^{16}O^{16}O^{16}O$ windows was 0.16 cm^{-1}. The window for $^{16}O^{16}O^{18}O$ was 1090.35 cm^{-1} with a width of 0,5 cm^{-1}.
(b) Several unresolved lines bet ween 1090.1 and 1090.6 cm^{-1}
(c) Sum of intensities between 1090,1 and 1090.6 cm^{-1}
(d) Average weighted by the intensities of the individual lines.

Table 3: **Error sources and resulting percentage uncertainties in retrieved column abundances from Table Mountain for a single spectrum**

Random Error Source	$^{16}O_3$	160160180
Finite signal-to-noise	().1 -1	0.1 -2.6
Error in 100% transmission level	2	2
Error in pressure-temperature profile	3	5
Error in fitting interfering lines	1	3
Error in assumed O_3 vertical distribution	5	5
Random error root sum of squares	**6.2 -6.3**	**7.9 -8.4**
Systematic Error Source		
Uncertainties in line intensity parameters	4	'20
Retrieval algorithm[1]	<5	<5
Total systematic error	<7	<21

1. This error tends to cancel out when retrieved mixing ratios are used to determine the enrichment.

FIGURE CAPTIONS

Figure 1: Previously reported and globally averaged ATMOS space-borne measurements of $^{50}O_3$ enrichment profiles. The error bars on the ATMOS measurements are the 10 standard deviations, and do not include systematic error. ATMOS altitudes are approximate and ATMOS $^{50}O_3$ enrichments are assumed to be the sum of (we-thirds the $^{16}O^{16}O^{18}O$ enrichment and cmc-(bird the $^{16}O^{18}O^{16}O$ enrichment. For **clarity, error** bars for many of the data points have been omitted, and altitudes for *Mauersberger* 11987], flight a, have been shifted upwards by 0.5 km. Data from *Carli and Park* [1988] are the range of their measurements. *Mauersberger* [*1981]:* O; *Mauersberger 11987], flight* a: o flight h: [1; *Abbas et al.* [*1* 987]: A; *Carli and* Park [1988]: ▩ ; *Scheueler et a/.* [*1 990]* flight 1: ▨, flight 11: ▧, flight III:=; ATMOS Spacelab 3 and ATLAS- 1, -2 and -3 average: —.

Figure 2: Spectral intervals used for space-hased profile retrievals of $^{16}O^{16}O^{18}O$ and $^{16}O^{18}O^{16}O$. The residual in the bottom panel was calculated as the fractional difference between the observed and the (not shown) calculated spectrum at 26.3 km.

Figure 3: $^{16}O^{16}O^{18}O$ and $^{16}O^{18}O^{16}O$ global and latitudinally-averaged enrichments from ATMOS space observations. All averages were done on a fixed pressure scale, and for clairity, the altitude shown is the average altitude at each pressure level in its particular latitude bin. All latitudinal averages were weighted by the inverse random error of the measurement and at least three observations were averaged for each point. The error ranges for the globally averaged profiles are the 1σ standard deviations. See text and *Gunson et al.* [this issue] for discussion of systematic errors. ATLAS-3 (Nov. 1994): ∇ 80°S-60°S, outside vortex; 80 °S-600S, inside vortex; + 0°-10°N; ☐ 10"N-30°N; A 30°N-60°N. ATLAS-2 (May 1993): ⊕ 60 °S-300S; ◿ 60°N-80°N, outside vortex; ⊞ 60°N-80°N, inside vortex. ATLAS-1 (Apr 1992): O 60 °S-300S; O 30 °S-10°S; ⋈ 1O"S-10"N; X 10 °N-30"N. Spacelab-3 (Apr 1985): ◺ -50°S; ▲ ≈30°N. ─── Global average; . 1σ standard deviation.

Figure 4: $^{48}O_3$ columns and column $^{16}O^{16}O^{18}O$ enrichments from Table Mountain. The error bars do not include systematic error (see text and Table 3.)

Figure   1

Figure 2
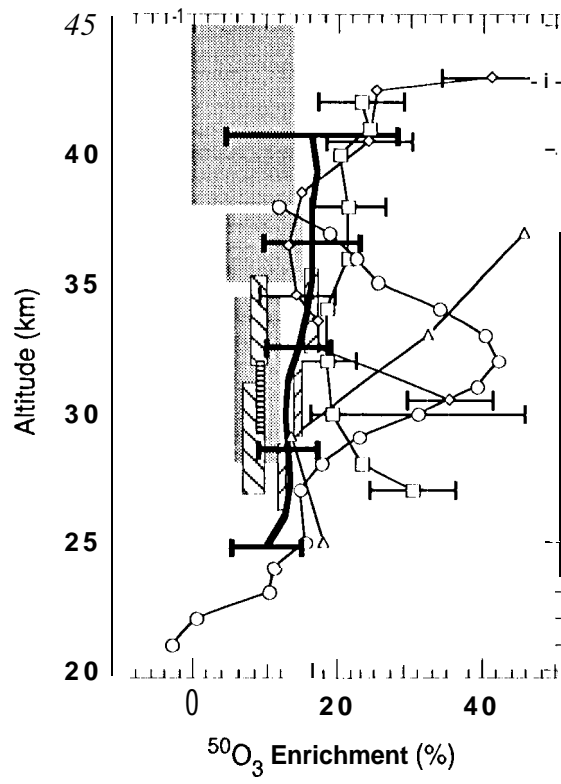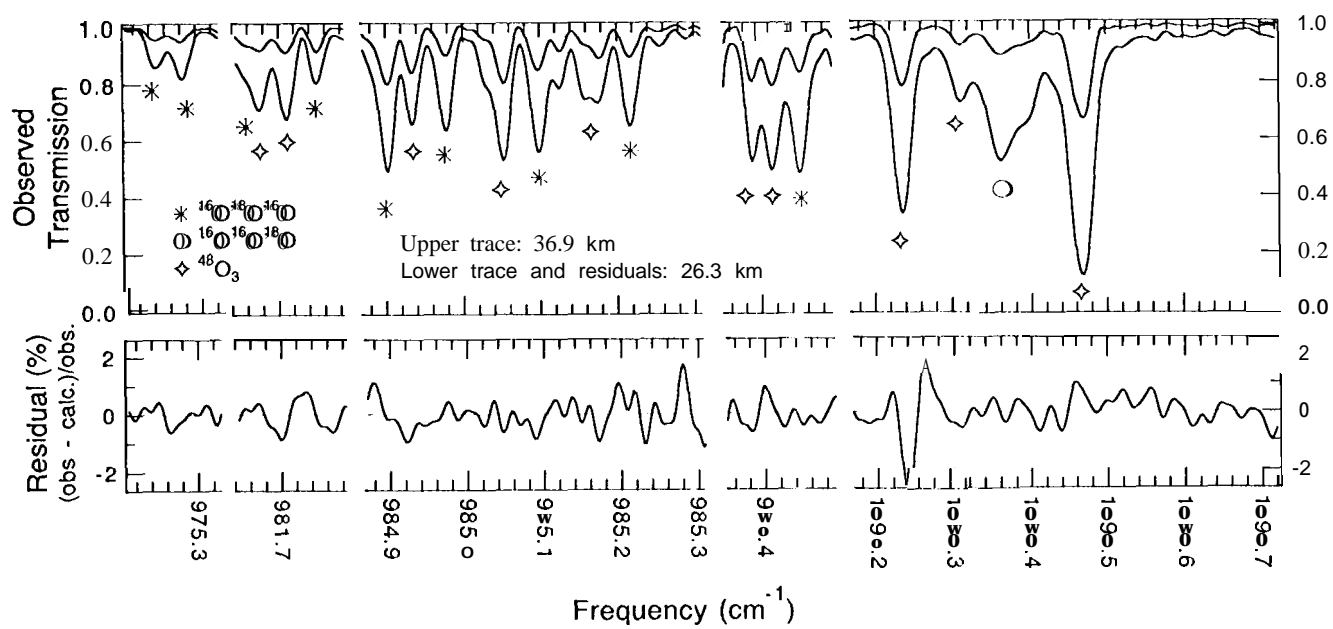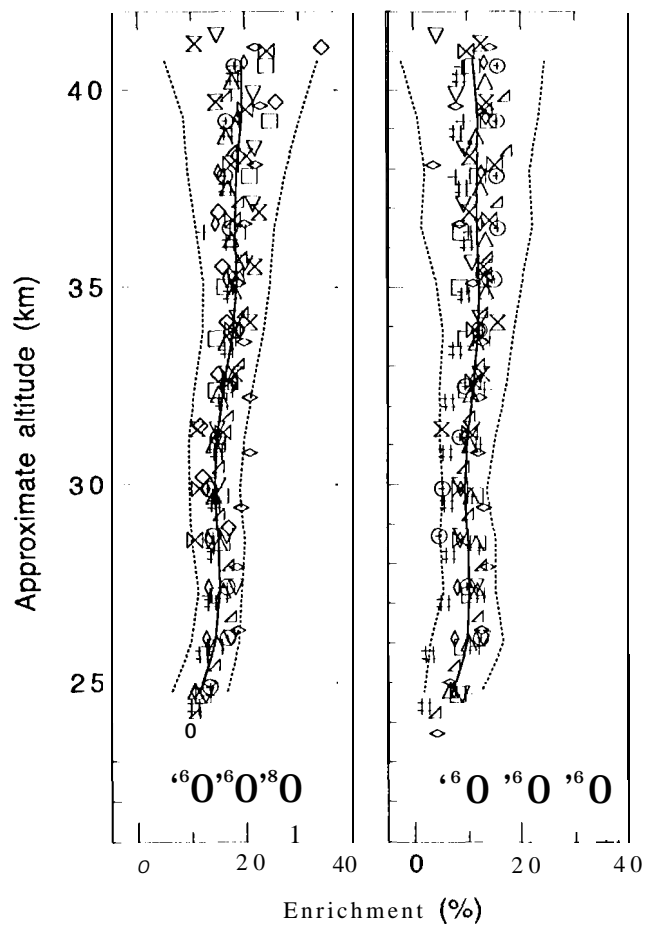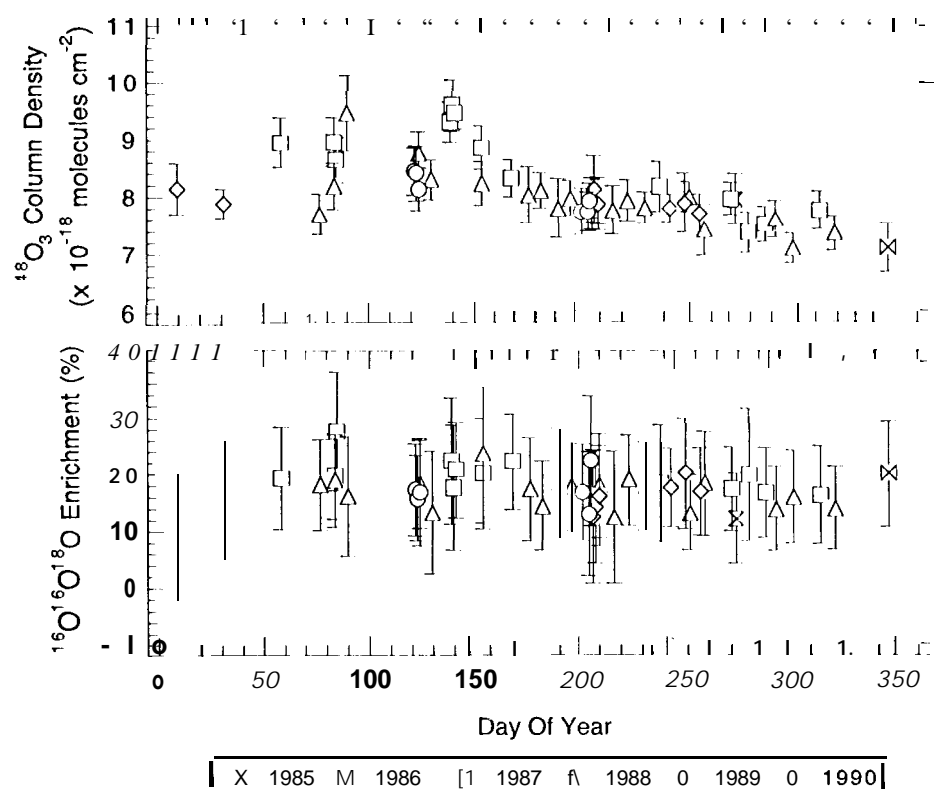
Figure 3

Figure 4